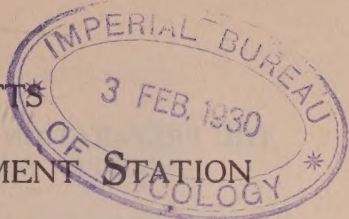


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The Preparation and Effectiveness of Basic Copper Sulfate as a Fungicide

By E. B. Holland, C. O. Dunbar, G. M. Gilligan and W. L. Doran

Copper fungicides have been a subject for investigation during the past few years. The work comprises a study of chemical composition, physical characteristics and general effectiveness in field work, together with the use of various supplementary products. The main objective was the preparation of a Bordeaux substitute that could be readily suspended in water and used as a spray, or mixed with a free-flowing carrier and applied as a dust. The product must give practical control of disease but not necessarily equal to a highly dispersed Bordeaux of the same copper content. The advantages of such a product in the saving of time, labor and equipment in preparation, and the gain in uniformity and stability of the spray mixture are evident. Since basic sulfates are generally considered preferable to basic carbonates, attention has been directed largely to them.

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AGRICULTURAL EXPERIMENT STATION,
AMHERST, MASS.

THE PREPARATION AND EFFECTIVENESS OF BASIC COPPER SULFATE AS A FUNGICIDE

By E. B. Holland, Research Professor of Chemistry, C. O. Dunbar and
G. M. Gilligan, Research Assistants in Chemistry, and
W. L. Doran, Research Professor of Botany

Basic copper sulfates are insoluble copper compounds resulting from the action of alkali or alkaline earth hydroxides or carbonates, short of saturation upon copper sulfate, although other precipitants are occasionally employed. The reaction has been studied by numerous chemists as shown in a previous paper (6, p. 741, 742)¹, but the lack of agreement, as a whole, tended to indicate the production of mixtures rather than a definite compound. When, however, the amount of precipitant was sufficient for complete precipitation of the copper, or nearly so, tribasic sulfate, $4\text{CuO} \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$, was frequently obtained. Proust (12, p. 34) prepared the compound with fixed alkalies; Kane (7, p. 270), with insufficient ammonia or potassium hydroxide; Smith (15, p. 498), with insufficient fixed alkalies and with sodium carbonate; Vogel and Reischauer (16), with ammonia; Field (5, p. 124), with insufficient fixed alkalies; and Pickering (10, p. 1982; 11, p. 1855), with fixed alkalies and with alkaline earths. More recently Bell and Taber (1, p. 173) and Young and Stearn (18, p. 1951, 1952) failed to obtain a definite salt by the phase rule, and Williamson (17, p. 790) secured unsatisfactory results but substantially the tribasic. Britton (3, p. 2152, 2153) by an electrometric determination with an oxygen electrode obtained a sodium hydroxide equivalent of 1.47 for copper sulfate which would indicate approximately $4\text{CuO} \cdot \text{SO}_3$. The alkali was added slowly with thorough agitation in order to secure the formation of an amorphous precipitate. With a copper electrode Britton (4, p. 2798) obtained an equivalent of 1.50 and by phase rule studies at 25° (4, p. 2800-2802) established a formula of $4\text{CuO} \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$. Bell and Murphy (2) by varying the quantity of copper sulfate with a given amount of copper oxide obtained in 8 hours at 100°C a neutral solution and the same basic sulfate. The results of Kruger (8) and Sabatier (14) tend to confirm the formula. The minerals brochantite and langite are said to be tribasic sulfates with three and four molecules of water respectively. Smith (15) obtained tetrabasic sulfate ($5\text{CuO} \cdot \text{SO}_3 \cdot 6\text{H}_2\text{O}$) short of alkalinity; and Pickering (10, p. 1982; 11, p. 1855), by adding alkali or alkaline earth hydroxide sufficient for initial alkalinity (1.60 mols). Nelson (9, p. 1189) obtained a basic sulfate of $7\text{CuO} \cdot 2\text{SO}_3$ previously reported by Proust (12, p. 34).

Preparation of Basic Copper Sulfate

With the exception of the preliminary experiments carbonates have been used as precipitants in the Station laboratory in preference to the hydroxides. The carbon dioxide evolved in the reaction prevents decomposition (blackening) in a measure, and the leavening effect of the gas seems to improve the physical condition of the resulting product. Precipitated calcium carbonate (CaCO_3), precipitated basic magnesium carbonate ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) and sodium carbonate (Na_2CO_3) have been employed for the purpose. The following commercial grades of precipitated calcium and magnesium carbonates are available according to the distributor:

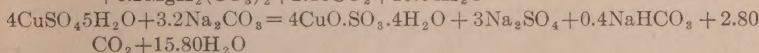
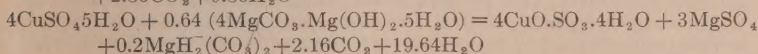
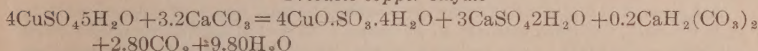
¹Reference is made by number to Literature Cited, p. 148.

Material	Cubic Inches in 1 Pound		
	Light	Medium	Heavy
Calcium carbonate.....	91	72	47
Basic magnesium carbonate.....	144	..	64

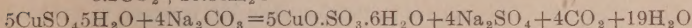
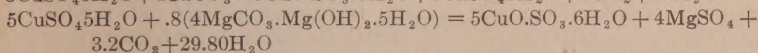
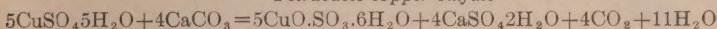
The light grades were employed as presumably offering greater surface area. The fine ground crystalline forms are cheaper but more resistant and less satisfactory. The solubility of both carbonates is low. Sodium carbonate, on the other hand, is readily soluble, and the crystalline sal soda with 10 molecules of water is as serviceable as the anhydrous and monohydrated forms. Soda ash might also be included if free from caustic alkali. Sodium carbonate is the least expensive, followed by precipitated calcium carbonate and basic magnesium carbonate. The cost, however, as with many other chemicals is largely dependent on the amount purchased, size and kind of containers.

The plan of operation adopted was based on complete precipitation of the copper with a minimum of precipitant. Pickering had shown previously that 1 mol of copper sulfate required 0.75 mol of a divalent hydroxide. In the case of carbonates 0.80 mol was invariably found necessary under the conditions employed. The following tentative reactions are offered:

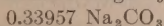
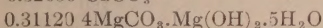
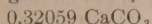
Tribasic copper sulfate



Tetrabasic copper sulfate



1 part by weight of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ requires:



The amount of precipitant found necessary would point toward the formation of tetrabasic sulfate (see Pickering), but as the amount of copper in the tri- and tetrabasic sulfates with 4 and 6 molecules of water respectively is 54.055 and 54.240 per cent, differentiation has to be based largely on the sulfuric acid content 17.020 and 13.663 per cent SO_3 . The analyses (page 127) of laboratory samples, prepared under conditions far short of theoretical control, would seem to indicate, however, that principally tribasic sulfate was formed together with more or less hydroxide when excess precipitant was employed or the mixing was inadequate. The 0.10 mol of precipitant (univalent) that did not react may represent the dilution at which the ionized sulfuric acid could not decompose the carbonates.

With the insoluble carbonates, hot dilute copper sulfate solution is run slowly into the suspended carbonate and stirred vigorously with a mechanical agitator throughout the operation; but with soluble carbonates, the carbonate is let down into the copper sulfate. The mix with insoluble carbonates should be slightly

alkaline to litmus and free from soluble copper (ferrocyanide test), basic copper carbonate, and oxidation products at the completion of the reaction. A neutral to slightly acid mix with a trace of soluble copper is more dependable when sodium carbonate is used and likely to yield a better product. The relative concentration, temperature, rate of addition and agitation should be so coordinated as to give a basic sulfate of the best physical characteristics possible. Similar results, however, may be obtained from different correlations. Allowing the precipitate to stand before filtering affects the bulk and increases the amount of carbonate, both of which are objectionable. The presence of iron in the copper sulfate also appears to injure the physical properties. A properly prepared basic sulfate is soft, pulverulent between the fingers, and free from grit and requires no grinding except the disintegration of the cake from the filter. Subsequent air separation, however, improves the physical properties especially for dusting purposes.

Commercial Preparation

The directions recently furnished a manufacturer for the preparation of basic sulfate with calcium carbonate are practically the same as originally published except as to size of the batch and the elimination of the excess precipitant. In adapting a laboratory process to factory conditions there is likely to be some loss in quality due to the limitations imposed by economic production.

1890 grams (4.17 lbs.) of copper sulfate, substantially free from iron, in 10 gallons of solution, heated to 80°C, are added gradually to 606 grams (1.34 lbs.) of light, precipitated calcium carbonate, suspended in 5 gallons of water, at 80°C, stirred *vigorously* for 30 minutes (including the time of precipitation) at 80°C, filtered immediately, washed practically free from soluble by-products, and dried at a relatively low temperature (35-50°C) to a soft, light, bulky, free-flowing, bluish powder of fine particles having a "fair" power of suspension and adhesiveness and containing about 26.50% of metallic copper.

The above batch yields nearly 4 pounds of material. Some of the gypsum is lost in the filtrate.

The method for preparing basic copper sulfate with precipitated basic magnesium carbonate is substantially the same as with calcium carbonate except that only 588+ grams (1.30 lbs.) are required when the carbonate holds true to formula. A preliminary trial with a few grams of material is advisable, however, to establish the proper ratio. Discoloration (blackening) is more likely to occur than with calcium, probably due to the basic portion of the carbonate. The discolored portion absorbs carbon dioxide rapidly on exposure to the air and is apparently converted into a blue basic carbonate which is considered inferior to the basic sulfate. The basic sulfate is a relatively pure, soft, blue, free-flowing powder of fine amorphous particles and contains about 53 per cent of metallic copper as the by-product, magnesium sulfate, is readily removed by washing. The batch yields about 2 pounds of material.

The method for preparing basic copper sulfate with sodium carbonate differs considerably from the calcium carbonate process in the concentrations employed, in the direct addition of the precipitant to the copper sulfate, and in the control necessary to coordinate the rate of addition with the efficiency in mixing. An undue concentration of the sodium carbonate causes the formation of a deep blue precipitate or a brown precipitate that absorbs carbon dioxide from the air and becomes more or less hard and gritty.

963 grams (2.12 lbs.) of anhydrous sodium carbonate (or 1127 grams (2.48 lbs.) of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, or 2600 grams (5.73 lbs.) of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) in 10 gallons of solution, heated to 70°C are added gradually to 2836 grams (6.25 lbs.) of copper sulfate in 5 gallons of solution at 70°C, stirred *vigorously* for 30 minutes (including the time of precipitation) at 70°C, filtered immediately and washed practically free from sodium sulfate and dried at a relatively low temperature (35-50°C) to a soft, adhesive, greenish-blue powder of fine amorphous particles containing about 53 per cent of metallic copper.

The sodium carbonate mix is the most difficult of the three to control but the color and reaction are fairly safe guides. The batch yields about 3 pounds of material.

Composition of Laboratory Samples

The analyses of two samples of basic copper sulfate prepared in the Station laboratory with an excess of calcium carbonate have been published (6, p. 747) but are again reported with a new hypothetical combination based on the theory of tribasic sulfate with the excess as copper hydroxide, which may or may not be more accurate. The theoretical composition, however, was merely incidental to the project and not pursued at length.

Basic Copper Sulfate

	Sample No. 1	Sample No. 2
	<i>Per cent</i>	<i>Per cent</i>
Water, 100°C	7.880	8.900
Cupric oxide, CuO	32.732	32.356
Copper, Cu	(26.150)	(25.850)
Calcium oxide, CaO	17.750	17.770
Carbon dioxide, CO ₂	0.803	0.805
Sulfur trioxide, SO ₃	30.980	30.790

Hypothetical Combination

Tribasic sulfate, 4CuO.SO ₃ .4H ₂ O	41.39	40.43
Copper hydroxide, Cu(OH) ₂	6.39	6.76
Calcium sulfate, CaSO ₄ .2H ₂ O	51.36	51.41
Calcium carbonate, CaCO ₃	1.83	1.83

As some of the hydrated compounds present were apparently unstable, the hygroscopic moisture determined is of little value and this may also account for the overrun in the calculations.

Another sample prepared with an excess of basic magnesium carbonate had the following composition:

Basic Copper Sulfate

	<i>Per cent</i>
Water, 103°C	0.694
Cupric oxide, CuO	67.316
Copper, Cu	(53.780)
Ferric oxide, Fe ₂ O ₃	0.025
Magnesium oxide, MgO	0.400
Carbon dioxide, CO ₂	0.939
Sulfur trioxide, SO ₃	16.180

Hypothetical Combination

Tribasic sulfate, 4CuO.SO ₃ .4H ₂ O	95.06
Copper hydroxide, Cu(OH) ₂	1.06
Copper carbonate, CuCO ₃ .Cu(OH) ₂	2.97
Ferric hydroxide, Fe(OH) ₃	0.04
Basic magnesium carbonate, 4MgCO ₃ .Mg(OH) ₂ .5H ₂ O	0.96

The product obtained with magnesium carbonate is more highly concentrated, as the magnesium sulfate is removed by washing, and tends to confirm the hypothesis as to formation of a tribasic salt.

Basic copper sulfate prepared with different carbonates varies somewhat in color, from batch to batch, but as a rule a greenish-blue to a light blue precipitate is preferable to a deeper colored product. After sieving, a good quality basic sulfate made from calcium carbonate should have a volume of 5 to 6 cubic centimeters to the gram; from magnesium carbonate, of about 3 c.c.; and from sodium carbonate, of about 2 c.c.

Character of the Commercial Product

From a chemical standpoint basic copper sulfate may be considered the active principle which together with gypsum and excess lime compose Bordeaux. The low basic sulfate prepared with calcium carbonate contains about 51+ per cent of gypsum while the high basic sulfate prepared with basic magnesium carbonate or sodium carbonate appears to be largely tribasic sulfate. Physically basic sulfate is not as highly dispersed as Bordeaux and therefore has a lower power of suspension, distribution (coverage), adhesiveness and general effectiveness. From the inception of the project the main objective was to prepare a Bordeaux substitute that could be readily dispersed in water and was substantially as effective in controlling diseases on vegetables and fruits as Bordeaux, but not necessarily of the same copper content. The use of basic sulfate as a dust has been of more recent application.

Since the Station laboratory is not equipped for quantity production, arrangements have been made, from time to time, with different chemical manufacturers to prepare basic copper sulfate for use in field work according to directions furnished. The G. Chem. Co. prepared low basic sulfate with calcium carbonate in 1925, two lots in 1926, and preliminary samples of high basic sulfate with basic magnesium carbonate in 1927. The M. Chem. Co. prepared high basic sulfate from sodium carbonate in 1927, and the C. Chem. Co. low and high basic sulfates with calcium carbonate and sodium carbonate, respectively, in 1928. Several manufacturers refused the work from lack of time, equipment or willingness to undertake a new product. With adequate tank agitators, rapid filtering apparatus, and other necessary equipment there does not seem to be any particular difficulty in producing basic sulfate, but without such facilities secondary reactions are likely to take place and more or less carbonate results. Furthermore, lack of adequate facilities generally injures the physical properties even more than the chemical, which is particularly objectionable in the case of copper fungicides where the size and character of the particles may be greater limiting factors in disease control than differences in composition. Basic sulfate, however, is generally acknowledged as being more efficient than basic carbonate of the same degree of dispersion. The absence of an appreciable amount of excess precipitant is to be noted in both high and low basic sulfates, and of by-products in high basic sulfate. The physical attributes sought are a soft, light, bulky, free-flowing product of fine amorphous particles having a high power of suspension in water, highly sustained air-floating properties as a dust, and good adherence to foliage and fruit. These characteristics are seldom attained in entirety but are more fully reproduced in the laboratory than in the factory in mass production. None of the firms appeared to have all the equipment needed to perform the work according to directions. The quality as a whole was rather inferior as judged by laboratory standards. In large measure the degree of dispersion is becoming recognized as the criterion and in practice is generally determined by suspension. The seven lots are summarized in Table 1.

The copper content of the several samples of low basic sulfate was fairly concordant and likewise those of the high basic sulfate. The amount of carbon dioxide indicates the presence of comparatively little carbonate except in three instances. As a whole the green-blue or light-blue lots seemed to be preferable to the darker colored. Most samples were soft, bulky and free from grit and of either a fibrous or powdery character. The fibrous samples were quite bulky and contained well developed spicules of calcium sulfate which were produced simultaneously with the basic sulfate and attached thereto, forming relatively large particles which agglomerated readily but did not pack. When the conditions

Table 1. Factory Prepared Basic Copper Sulfate

Lab. No.	Manu- facturer	Basic copper sulfate	Copper content <i>Per cent</i>	Carbon dioxide <i>Qualitative</i>	Color	Volume per gram <i>c. c.</i>	Flow	Size of particles <i>Microns</i>	Remarks
1	G—	low	26.38	slight	blue	5.14	powdery	5.4	more amorphous than crystalline
2	G—	low	26.50	trace	light blue	7.60	powdery, slightly fibrous	7.2	crystalline
3	G—	low	26.31	slight	light blue	6.47	powdery	5.3	amorphous or too slightly crystalline to detect
4	G—	high	53.31	trace	green-blue	2.95	powdery	2.1	amorphous, slightly gritty
5	M—	high	52.95	trace	green-blue	2.14	powdery	3.6	amorphous
6	C—	low	26.45	much	dirty green	2.19	powdery, flourlike	5.6	amorphous or too slightly crystalline to detect
7	C—	high	52.56	much	dirty green	1.54	powdery, flourlike	2.9	amorphous
<i>Samples in composite</i>									
a	30	low	26.15	sl. trace	blue	<i>Laboratory samples for comparison</i>		7.1	crystalline
b	26	low	25.85	sl. trace	blue	12.32	fibrous, agglom- erates	8.2	crystalline
c	4	low	25.85	trace	deep blue	10.12	fibrous, agglom- erates	5.9	crystalline
d	11	low	none	light blue	8.92	powdery	2.3	amorphous, gypsum spicules present
e	15	low	trace	green-blue	6.25	powdery, slightly fibrous, agglom- erates	3.4	amorphous
f	22	high	53.78	trace	blue	5.63	powdery	5.5	amorphous
g	6	high	much	green-blue	3.25	powdery	1.8	amorphous
h	4	high	none	deep blue	1.87	powdery, sticky	2.0	amorphous
i	1	high	53.55	slight	green-blue	4.42	powdery	2.3	amorphous
j	2	high	blue	1.72	powdery	1.8	amorphous

Nos. 1, 2, 3, 6, a, b, c, d and e were prepared with calcium carbonate.

Nos. 4 and f were prepared with magnesium carbonate.

Nos. 5, 7, g, h, i and j were prepared with sodium carbonate.

of precipitation did not permit the growth of crystals, the product was powdery and the particles amorphous or too slightly crystalline to be detected. All the samples of high basic sulfate were amorphous. Nearly all the samples except the flourlike showed a fair flow in the bottle but poor on a pane of glass, and the fibrous were inferior to the powdery. The adhesive power of the fibrous samples to glass was also inferior to the powdery, and sample "g" with particles of 1.8 microns in size the most promising.

Field Work in 1925 with Commercial Basic Copper Sulfate

Attention has been called (6, p. 748) to the relative effectiveness of laboratory prepared basic copper sulfate and of Bordeaux with various spores as determined by W. L. Doran of the department of botany of this Station, using the method of Reddick and Wallace (13). Slightly greater concentration (copper content) of basic sulfate than of Bordeaux was required to inhibit the germination of the more resistant fungi. In addition (6, p. 749-750) field experiments were conducted in 1925 by E. F. Guba of the Market Garden Field Station at Waltham, Mass., to determine the relative effectiveness of basic copper sulfate (lot 1) and of Bordeaux 4-4-50 in controlling anthracnose and downy mildew on cucumbers and early and late blights on celery. Observations and yields indicate that basic sulfate was substantially as effective, per unit of copper, as Bordeaux in both instances.

Field Work in 1926

The field work of 1926 with basic sulfate includes experiments with cucumbers and celery at the Market Garden Field Station at Waltham, with potatoes on the farm of E. S. Fulton at North Amherst, and with apples, plums and grapes in the College orchard and vineyard. The experiments with cucumbers and celery were conducted by E. F. Guba as in the previous year.

Cucumbers

The cucumber experiment consisted of 3 plots, 132 by 12 feet, of 2 rows each, planted in hills 6 feet apart each way. The seed was sown three times and that of June 16 finally gave a successful stand. The plants were sprayed before vining by a knapsack sprayer and later by a Bean Truck or Arlington X. L. sprayer with Friend nozzles under 200 to 250 pounds pressure. Frequent applications were necessary on account of rains. Lead arsenate and lime 2-2-50 were applied on July 7, 15, 20 and 26 for the striped beetle. Vining began about August 2. Basic sulfate (lot 2) 3.84-50 and Bordeaux 4-4-50 with lead arsenate 2-50 were applied on August 2, 5 and 11; the fungicides alone on August 17 and 25, and the fungicides with one-half pint of nicotine sulfate for green aphids on September 1. The basic sulfate was mixed with approximately 6.17 ounces of Wilkinit and 0.88 ounces of crude saponin to increase wetting, spreading and adhesiveness. The cucumbers were inoculated with anthracnose fungus, *Colletotrichum lagenarium* (Pass.) Ells. and Hals., on August 17 and 27. The fungicides were prominent on the foliage at the time. Powdery mildew, *Erysiphe cichoracearum* D. C., appeared naturally and developed on the check plot.

The season was unfavorable for cucurbits, due to poor growing conditions and a fairly general infestation of mosaic, bacterial wilt, striped beetles and green aphids which affected both the stand and the yield. Leaf counts made on September 8 and 10 may serve, however, to indicate the relative effectiveness of the two fungicides.

Table 2. Relative Effectiveness of Basic Copper Sulfate and Bordeaux in Controlling Anthracnose of Cucumbers

Fungicide	Copper content	Number of applications	Total leaves	Healthy leaves	Diseased leaves	
	Per cent		No.	No.	No.	Per cent
Basic copper sulfate 3.84-50..	0.25	10	1251	1215	36	2.88
Bordeaux mixture 4-4-50. . . .	0.25	10	1544	1496	48	2.98
Check.....	0.00	0	1857	1221	636	31.25

In conclusion Guba states that basic copper sulfate showed no inferiority to homemade Bordeaux in the control of anthracnose on cucumbers. Both readily controlled powdery mildew which was apparent on practically all leaves in the check. Both fungicides appeared to be equally toxic to young cucumber leaves although the injury could not be considered serious.

Celery

The celery experiment consisted of 4 plots, 64 by 12 feet, of 4 rows, 3 feet apart, each. The plants were raised in a seed bed and set out on July 15. Basic copper sulfate (lot 2) 3.84-50 and Bordeaux 4-4-50 were applied on June 25 to the plants in the seed bed when 1.5 inches high, and again on July 9; in the field on August 2, 5, 11, 17 and 25 and September 1, 9 and 21. Nicotine sulfate was added on September 9. The basic sulfate was applied both with and without the combined spreader.

A knapsack sprayer was used in the seed bed and in the field a Bean Truck or Arlington X. L. sprayer with Friend nozzles under 200 to 250 pounds pressure covering 4 rows, 3 nozzles to a row. The entire planting was inoculated with a spore suspension of *Cercospora apii* Fries and *Septoria apii* (Br. and Cav.) Rost. on the nights of September 9 and 21, following treatments. The celery was boarded on October 7 and harvested on October 19 and 25, at which time leaf counts were made of the two interior rows of each plot.

Table 3. Relative Effectiveness of Basic Copper Sulfate and Bordeaux in Controlling Early and Late Blights of Celery

Fungicide	Copper content	Number of applications	Total leaves	Healthy leaves	Diseased leaves	
	Per cent		No.	No.	No.	Per cent
Basic copper sulfate 3.84-50..	0.25	10				
Leaf count Oct. 19.....			5468	5400	68	1.24
Oct. 25.....			2310	2258	52	2.25
Mean.....						1.54
Basic copper sulfate 3.84-50, with spreader and adhesive	0.25	10				
Leaf count Oct. 19.....			4232	4171	61	1.44
Oct. 25.....			2272	2200	72	3.17
Mean.....						2.04
Bordeaux mixture 4-4-50. . . .	0.25	10				
Leaf count Oct. 19.....			4054	3960	94	2.32
Oct. 25.....			3035	2965	70	2.31
Mean.....						2.31
Check.....	0.00	0				
Leaf count Oct. 19.....			4930	2793	2137	43.35
Oct. 25.....			2366	1467	899	38.00
Mean.....						41.61

From the leaf counts made on October 25, early blight was rather more prominent on the sprayed plots and late blight on the check. The celery from the treated plots was excellent with a negligible percentage of infection. That from the check plots showed considerable early and late blights, confined largely to the outer leaves, which did not materially affect its value. The basic sulfate without spreader was fully as effective as with the combined spreader or as Bordeaux. Saponin increased wetting and spreading, but Wilkinité proved of no particular value unless possibly to increase visibility (Guba).

Potatoes

Experiments were conducted on the farm of E. S. Fulton at North Amherst under the supervision of W. L. Doran of the department of botany of this Station to determine the relative effectiveness of basic copper sulfate and of Bordeaux in controlling early and late blights on potatoes. Uncertified Green Mountain seed was used without disinfecting. The fungicides were basic copper sulfate (lot 3) 4-50 with combined spreader and homemade Bordeaux 4-4-50, to which was added lead arsenate when necessary for the control of the Colorado potato beetle. Applications were made on July 15 and 26 and August 9 and 18 with a Yellow Jacket equipment under a pressure of 175 pounds, 2 nozzles to a row, and about 90 gallons to the acre. Leaf hopper or tipburn injury, leaf-roll and late blight were the principal infestations of the season. Leaf hoppers were very prevalent and no nicotine sulfate was employed. Early blight was inappreciable; late blight was late in appearing and probably did not constitute a serious factor. On harvesting there was not over 1 or 2 per cent of tuber rot. The yield was calculated from the weight of the two inside rows (equivalent to $\frac{1}{2}$ acre) in each plot on the basis of marketable potatoes, 60 pounds to the bushel.

Table 4. Relative Effectiveness of Basic Copper Sulfate and Bordeaux in Controlling Early and Late Blights of Potatoes—As Shown by Yields

Fungicide	Copper content	Number of applications	Number of rows treated	Yield per acre	Gain or loss over check	
	Per cent			Bu.	Bu.	Per cent
Basic copper sulfate 4-50						
East plot.....	0.25	4	8	190.4	-6.4	-3.25
West plot.....	0.25	4	8	189.6	-7.2	-3.66
Average.....				190.0	-6.8	-3.46
Bordeaux mixture 4-4-50						
East plot.....	0.26	4	8	192.0	-4.8	-2.44
West plot.....	0.26	4	8	217.6	+20.8	+10.57
Average.....				204.8	+8.0	+4.07
Check.....	0.00	0	4	196.8

Observations and yields indicate that basic sulfate was rather less efficient in controlling late blight than Bordeaux, although only one of the sprayed plots showed an increase in yield over the check. Furthermore, the number of applications would have been decidedly inadequate in so rainy a season had blights appeared earlier.

Fruits.

Experiments were conducted in the College orchard and vineyard under the supervision of J. K. Shaw and O. C. Roberts to determine disease control and foliage injury of basic sulfate on Baldwin and McIntosh apples, Monarch plums and Moore's early grapes. The highest concentration employed was 4 pounds to 50 gallons with combined spreader. Concentrations of 3 and 2 pounds were

obtained by increasing the dilution of the previous mixture. For apples a large-sized Friend spray apparatus, under 300 pounds pressure, with two Boyce guns, parallel nozzles and $\frac{5}{16}$ -inch discs was used. Prepink (May 7), pink (May 13), and calyx (June 2) applications were made of about 6 gallons to a tree. Basic sulfate failed to control scab as effectively as liquid lime-sulfur, injured the foliage and russeted the fruit. The latter was not particularly serious with the lowest concentration.

For plums and grapes a 50-gallon hand outfit, under approximately 175 pounds pressure, equipped with rod and disc nozzle, was employed. The plums were sprayed on May 24 and June 8 and the grapes on May 19, June 8 and July 17. Roberts reported that the spreading and adhesiveness of basic sulfate appeared to be satisfactory. The effectiveness could not be determined as there was practically no disease present. Foliage injury was observed on all the plants sprayed, increasing with concentration, but evidently was not appreciable on the fruit of plums and grapes.

Miscellaneous

Dr. W. P. Brooks of Amherst sprayed currants, English gooseberry, nine varieties of grapes, tea roses and phlox with basic sulfate 4-50 with combined spreader and did not observe any foliage injury.

L. F. Kinney of Kingston, Rhode Island, sprayed seedlings of *Rhododendron Cataubiense* in flats with basic sulfate 2.5-50 without injury.

Field Work in 1927

The field work of 1927 with basic copper sulfate includes experiments with cucumbers and celery at the Market Garden Field Station at Waltham, with potatoes on the Experiment Station plots at Amherst and on the farm of G. Fred Pelissier at Hadley, and with apples and grapes in the College orchard and vineyard. The basic sulfate was applied both as a spray and mixed with a free-flowing talc as a dust. The experiments with cucumbers and celery were conducted by E. F. Guba as in previous years.

Cucumbers

The objective was to determine the relative efficiency of spray and dust applications of basic sulfate in controlling anthracnose and mildews on cucumbers. The experiment consisted of 3 plots, 120 by 12 feet, of 2 rows each, planted in hills 6 feet apart each way. Several preliminary treatments were found necessary to control insects. Bordeaux 4-4-50 was applied for flea beetles after the first leaves appeared (June 8); sodium fluosilicate dust for striped beetles on June 17, 21 and 30 and July 8; and lead arsenate, lime and nicotine sulfate 1.50-2-0.5 pt. 50 for striped beetles on July 14. The regular spray consisted of basic sulfate (lot 5), lead arsenate and raw linseed oil 2-1.5-0.5 pt. 50 and contained about 0.26 per cent copper and 0.07 per cent arsenic. The dust consisted of basic sulfate (lot 5), lead arsenate and talc and contained about 7.02 per cent copper and 4.01 per cent arsenic. The plants were treated on July 21 when vining began and on July 28 and August 4. A 3-gallon knapsack sprayer and a 2-quart Feeney duster were employed for application. The spray left a thin, hardly perceptible residue which disappeared entirely after the least rainfall. The oil was not found satisfactory as a spreader or adhesive. Dusting resulted in a heavy deposit on the foliage and protection of the lower surface of the leaves. Neither application caused perceptible injury. The vines made a poor growth due to severe stunting and foliage injury resulting from applications of sodium fluosilicate from which

they did not recover and also from inability to control the striped beetles and accompanying mosaic. The cucumbers were inoculated with a spore suspension of anthracnose, *Colletotrichum lagenarium* (Pass.) Ells. and Hals., on July 21, and leaf counts made on August 11.

Table 5. Effectiveness of Basic Copper Sulfate in Controlling Anthracnose of Cucumbers

Form of application	Copper content	Number of applications	Total leaves	Healthy leaves	Diseased leaves	
	<i>Per cent</i>		<i>No.</i>	<i>No.</i>	<i>No.</i>	<i>Per cent</i>
Spray.....	0.26	3	374	29	345	92.25
Dust.....	7.02	3	461	88	373	80.91
Check.....	0.00	0	340	30	310	91.18

Dr. Guba reported that it was impossible to maintain protection this season due to continuous heavy rains. The dust, however, appears to have afforded slight protection.

Celery

Three plots, 120 by 12 feet, of 4 rows, 3 feet apart, each, were employed. The spray consisted of basic sulfate (lot 5) and raw linseed oil 2-0.5 pt.-50 and contained about 0.26 per cent copper. The oil proved unsatisfactory but was omitted only on August 26. The dust consisted of basic sulfate (lot 5) and talc and contained about 7.02 per cent copper. Treatments were made on August 10, 17 and 26 and September 2, 12 and 20. The celery was inoculated with a spore suspension of early and late blights on August 26, boarded on September 26, harvested on October 14 to 16 and the yield of marketable celery determined.

Table 6. Effect of Basic Copper Sulfate on the Yield and Grade of Celery

Form of application	Copper content	Number of applications	Number of Bunches			Increase over check
			Grade 1	Grade 2	Total	Total bunches
	<i>Per cent</i>					<i>Per cent</i>
Spray.....	0.26	6	163	45	208	38.67
Dust.....	7.02	6	192	26	218	45.33
Check.....	0.00	0	93	57	150

Grade 1: 3 good sized stalks to the bunch, 18 bunches to the box.

Grade 2: 4-7 small stalks to the bunch, 18 bunches to the box.

The yield and the grade were increased by the use of basic sulfate, particularly the dust.

Potatoes

Dusting experiments were conducted on the Station rotation 0.05 acre plots Nos. 7, 17, 53, 54 and 55 and 0.03 acre intervening strips under the supervision of J. P. Jones to determine the effectiveness of basic copper sulfate in controlling early and late blight on potatoes. The seed was Massachusetts certified (Green Mountain, grown in Charlemon and disinfected with corrosive sublimate. The seed was planted on May 7, and the crop harvested on September 16. The cultural and fertilizer treatment was of the usual character. The plots were dusted on June 16 and 25, July 1, 8, 19 and 29 and August 6 with a mixture of basic sulfate (lot 5), lead arsenate and talc containing about 7.52 per cent copper and

4.00 per cent arsenic. The mixture applied on July 29 did not contain arsenic. The amount of dust required increased with the growth of the plants but averaged about 48.10 pounds an acre for each treatment. The persistence of the Colorado potato beetle necessitated the continued use of arsenic. Two per cent nicotine dust was applied on July 27 and August 3 at the rate of about 20 pounds an acre but did not prove particularly effective. Weather conditions and ladybugs, however, prevented the rapid spread of aphids and leaf hoppers were not abundant (A. I. Bourne). Foliage injury was inappreciable as a whole although occasionally burning was observed where a large amount of dust accidentally lodged on the plant (J. P. Jones). For applying the dusts two hand dusters, the American Beauty and the double action Cheeseman, were tested and gave "fair" distribution, but the former was considered easier to operate and was employed.

Growth was excellent until July 19, when yellowing of the lower leaves was observed, apparently due to age or to excessive shading by the dense growth of vines, as there was no evidence of disease and leaf hoppers and aphids were not particularly destructive. By August 6 most of the leaves were severely injured by tip burn and on August 20 nearly all were dead (Jones). The amount of early blight was negligible but some late blight appeared about the first of September after most of the foliage was dead and caused 1 to 2 per cent of tuber rot (Doran). The yield of the several plots is reported on the basis of 60 pounds to the bushel.

Table 7. Yield of Potatoes on the Rotation Plots. (Per Acre.)

Location of plots	Total Yield	Grade 1	Grade 2	Grade 3	Rotted	Rotted
	<i>Bu.</i>	<i>Bu.</i>	<i>Bu.</i>	<i>Bu.</i>	<i>Lbs.</i>	<i>Per cent</i>
On high ground.....	241.8	121.3	79.8	40.3	22.5	0.16
On slope.....	199.2	99.4	60.0	36.2	213.3	1.81

Grade 1: All disease free potatoes above 1.75 inches in diameter.

Grade 2: All disease free potatoes above 1 inch in diameter, not included in Grade 1.

Grade 3: All disease free potatoes 1 inch or under in diameter.

The low yield has been ascribed to leaf hoppers and aphids (Jones) and to the effect of previous crops (Snell). The fact that the yield was appreciably larger and the amount of rot less on the plots which were better located as to elevation and natural drainage (Snell) would seem to indicate that the abnormal precipitation during August was a limiting factor. As there were no check plots the effectiveness of the dust must be judged largely from observations of the foliage and the amount of tuber rot.

A spraying experiment was conducted on the farm of G. Fred Pelissier at Hadley (8 acres) to determine the relative effectiveness of basic copper sulfate and Bordeaux in controlling early and late blights on potatoes. The seed was certified Rural Russets, raised by K. C. Livermore of Honeoye Falls, New York, and disinfecting with corrosive sublimate. Planting was begun on May 4. The entire field received similar cultural and fertilizer treatment and was sprayed seven times from June 27 to September 9 at the rate of 100 gallons an acre. To the major portion of the field was applied a mixture of Bordeaux 4-50 and lead arsenate 2-50 containing about 0.24 per cent copper and 0.09 per cent arsenic. Chemical hydrated lime or finishing lime (Tiger Brand) was used in place of quicklime, pound for pound, in preparing the Bordeaux. To an inner strip of one acre was applied a mixture of basic sulfate (lot 5), lead arsenate and raw linseed oil 2-2-0.5 pt.-50 containing about 0.25 per cent copper and 0.09 per cent arsenic.

A traction field force pump of 100 gallons capacity with a boom covering 4 rows, 3 nozzles to a row, was employed. Repeated use of lead arsenate was found necessary to check the Colorado potato beetle. Leaf hoppers were not prominent and aphids constituted a minor factor; nevertheless, two treatments of nicotine sulfate were applied to one acre but the results did not warrant the added expense (Pelissier). W. L. Doran observed some late blight but "not over 1 or 2 per cent of late blight rot in the entire field regardless of the fungicide used." A considerable number of vines were still green when the crop was harvested on October 10. The yield calculated from a single determination of 5 rods, of 2 rows each, was 301.8 bushels an acre for basic sulfate and 451.7 bushels for Bordeaux. Neither the life of the vines nor the amount of disease could account for any such differences.

Apples

A spraying experiment was conducted on Block E of the Station orchard under the supervision of J. K. Shaw and W. L. Cutler to determine the relative effectiveness of basic sulfate and lime-sulfur in controlling scab on McIntosh and Baldwin apples and the amount of injury. A mixture of high and low basic sulfates (lots 4 and 2) was employed in two concentrations, dilute and triple-strength. Whenever the low basic sulfate was used, in whole or in part, the amount was doubled. The dilute mixture consisted of basic sulfate, lead arsenate and saponin 0.50 1.50-0.055¹ 50 and contained about 0.06 per cent copper and 0.07 per cent arsenic. In the third and fourth applications raw linseed oil 0.50 pt.-50 was substituted for saponin. The triple-strength mixture was the same as the dilute except as to copper content and contained about 0.19 per cent copper. A standard mixture of liquid lime-sulfur, lead arsenate and calcium caseinate 1.25 gals. 1.5 0.5 50 was applied to similar trees for comparative purposes. A Friend power sprayer with 250-gallon tank under 275 pounds pressure and Friend guns with $\frac{3}{32}$ disc nozzles were employed for the several mixtures. Care was taken to cover the trees thoroughly but to avoid drenching.

In the pre-pink spray (April 21) the dilute basic sulfate mixture with saponin injured the fruit buds a little, about the same as lime-sulfur, but the concentrated damaged the buds seriously. In the pink spray (April 25) the dilute mixture with saponin injured the buds slightly more than lime-sulfur, but the concentrated killed the buds and injured the young leaves. In the calyx spray (May 19) the dilute mixture with linseed oil caused less injury than lime-sulfur. The use of the concentrated was discontinued. A later application (July 1) of the dilute mixture with linseed oil substantiated previous results. The oil dispersed readily in the mixture and increased adhesiveness. McIntosh foliage is particularly sensitive to copper injury. Trees with 85 per cent bloom, set 71 per cent with dilute basic sulfate and 88 per cent with lime-sulfur. Very little or no scab was observed with basic sulfate or lime-sulfur.

A dusting experiment was conducted in the College orchard under the supervision of Brooks D. Drain to determine the effectiveness of basic copper sulfate in disease control on McIntosh apples and Bartlett pears and the amount of injury. High and low basic sulfates (lots 5 and 2) were employed in two concentrations, dilute and double-strength. The dilute mixture consisted of basic sulfate, lead arsenate, and talc and contained about 2.50 per cent copper and 2 per cent arsenic. The double-strength contained about 5.00 per cent copper but was otherwise the same. Crude saponin, 1 pound in 100, was incorporated in both mixtures applied on May 7 and June 2 to apples and on June 2 to pears but was excluded from the mixtures applied on August 5 to apples and pears.

¹25 grams.

Drain reported that with both dusts there was a small amount of russet on McIntosh apples but no foliage injury. A few scab spots were detected on trees receiving the dilute mixture. Bartlett pears showed neither scab nor injury. In addition Drain stated that the dust distributed well, and appeared to have good adhesiveness.

Grapes

Experiments were conducted in the College vineyard, under the supervision of O. C. Roberts, to determine the relative effectiveness of spray and dust applications of basic copper sulfate. Lots 5 and 2 and of Bordeaux 4-4-50 in disease control and foliage injury on grapes. Two concentrations of sprays and two of dusts with lead arsenate in all cases were employed as with apples. Crude saponin 25 gms. 50 was used in the first three spray applications and raw linseed oil 1 pt. 50 in the fourth. Crude saponin 1 pound in 100 was incorporated in the first three dust applications and omitted in the fourth. The variety Winer, was used in the tests. The vines, located in a portion of the vineyard where conditions were relatively uniform, were divided into 6 groups, plots, of 3 rows each, with approximately 9 vines to a row. Five plots received dilute and concentrated sprays, dilute and concentrated dusts, and Bordeaux, respectively. The sixth served as a check. The details of the treatments were as follows:

Fungicide	Copper Content Per cent	Number of Applications	Amount of Material
Dilute spray.....	0.06	4	35.5 Gals.
Concentrated spray.....	0.19	4	37.0 Gals.
Dilute dust.....	2.50	4	8.0 Lbs.
Concentrated dust.....	5.00	4	7.5 Lbs.
Bordeaux.....	0.24	4	35.5 Gals.
Check.....	0.00	0	0.0

Spray and dust treatments of basic sulfate were applied when the first leaves were about to appear (May 14, when the shoots were about 12 inches long June 11, when the grapes were about the size of peas July 18, and when the grapes were from $\frac{1}{2}$ to $\frac{3}{4}$ grown August 11. The weather conditions at the time of application were as follows:

May 14—clear, no wind, 53° Fahr.
 June 11—partly cloudy, light breeze, 70° Fahr.
 July 18—clear, light southerly breeze, high humidity, 65° Fahr.
 August 11—partly cloudy, no wind, 65° Fahr.

The Bordeaux was applied on May 14, June 10, July 12 and August 11. The sprays were applied under 75 to 100 pounds pressure with a double action. Daming barrel hand pump equipped with two lines of hose to which were attached rods and disc nozzles. The dusts were applied with an American Beauty hand duster. The adhesiveness of the spray was considered poor, partly due, it is believed, to the similarity in color of the spray residue and foliage, while that of the dusts was highly commended.

The concentrated spray and dust caused considerable injury to the foliage, the dilute spray a little and the dilute dust practically none. The leaves remained green 10 to 14 days longer than with Bordeaux and complete defoliation was delayed fully as many days. The Bordeaux was the most injurious of all treatments and the "burned" condition of the foliage was decidedly apparent. This may have been due to carbonating of the lime. The rainfall during the summer was comparatively high and the temperature low. Some mildew was detected on the check rows during the latter part of August and the first of September, but no black rot was observed on any vines. There was not sufficient disease present

at any time to constitute a real test of the fungicides. The fruit was of good quality from all vines including the checks, and there seemed to be no appreciable injury from the various treatments. The yields are not reported on account of pilfering of the fruit.

Field Work in 1928

The field work of 1928 with basic sulfate includes experiments with celery on the vegetable garden plots at the College, with potatoes on the Experiment Station plots and on the College farm, and with apples and grapes in the College orchard and vineyard. Low and high basic sulfates were employed in both spray and dust applications.

Celery

Spraying and dusting experiments were conducted on the College grounds, under the supervision of G. C. Stout, to determine the relative effectiveness of low and high basic sulfates (lots 6 and 7), Bordeaux 4-4-50 and a commercial monohydrated copper sulfate-hydrated lime dust (copper-lime dust) in controlling early and late blights on celery. The basic sulfates with raw linseed oil 1.25 pts.-50 as a spreader and sticker were applied as sprays at a concentration of 0.24 per cent copper, the same as Bordeaux 4-4-50. The basic sulfates mixed with a free-flowing tale were applied as dusts which contained 6.80 per cent copper, the same as the guarantee of the copper-lime dust. The sprays were applied with a barrel pump under about 75 pounds pressure and the dusts with a Niagara hand duster. The field was divided into plots of 4 rows each to which the several fungicides were applied, and 2½ rows for checks. The celery plants (Giant Pascal) were set rather late and made a poor growth due to unfavorable weather conditions. The fungicides were applied on July 30, August 9, 21 and 31 and September 28. Doran observed late blight on August 18 but no difference between plots. On October 29 there was late blight on the older leaves of all plots. No copper injury was noted. From general appearance [the sprays were the most effective, followed by the dusts and checks. Bourne] observed a few plant lice equally distributed. The celery [did not reach marketable size, but the two middle rows of each plot were pulled and weighed for yield records.

Table 8. Relative Effectiveness of Low and High Basic Sulfates, Bordeaux and Copper-lime Dust in Controlling Early and Late Blights of Celery,—As Shown by Yields

Fungicide	Copper content	Number of applications	Yield	Increase over check
	<i>Per cent</i>		<i>Lbs.</i>	<i>Per cent</i>
Low basic sulfate spray.....	0.24	5	206	145.24
High basic sulfate spray.....	0.24	5	228	171.43
Bordeaux 4-4-50.....	0.24	5	273	105.95
Check (one row only)	0.00	0	42
Low basic sulfate dust.....	6.80	5	94	20.51
High basic sulfate dust.....	6.80	5	102	30.77
Commercial copper-lime dust....	6.80	5	138	76.92
Check (one row only).....	0.00	0	39

There were no replications and the plots suffered unequally from adverse weather conditions so that the experiment has little significance except to indicate that 0.24 per cent sprays were more effective than 6.80 per cent dusts.

Potatoes

A spraying experiment was conducted on a 3.55 acre strip on the Farm field north 1, under the supervision of M. H. Cubbon, to determine the relative effectiveness of low and high basic sulfates (lots 6 and 7) and Bordeaux 4-4-50 in controlling early and late blights on potatoes. The field was undulating from east to west and suffered from excessive water in the dips. It was divided into 2 sections (156 by 495 feet), east and west, of 13 four-row plots each. The east half was evidently more uniform than the west. The entire field was manured at the rate of 15 tons to the acre, and in addition the east half received 1100 pounds an acre of a high commercial fertilizer and the west half 600 pounds of the same mixture. The seed was certified Green Mountain disinfected with corrosive sublimate. The potatoes were planted on May 14 and 15 at the rate of 25 bushels an acre on the two southern rows of each plot 1 to 9 inclusive and 15 bushels an acre on the northern rows of plots 1 to 9 and all rows of plots 10 to 13 inclusive. The crop was harvested between September 17 and October 10. The basic sulfates with linseed oil 0.50 pt.-50 were applied at a concentration of 0.24 per cent copper, the same as Bordeaux 4-4-50 and with lead arsenate 2-50 when necessary. Chemical hydrated lime was used in preparing the Bordeaux. A "Gray Jacket" traction field force pump with a 100-gallon tank, under 200 to 300 pounds pressure, and a boom covering 4 rows, 3 nozzles to a row, was employed. The amount of spray varied somewhat with the pressure from 100 to 135 gallons an acre. The plants were slow in starting but made a fair growth considering the season. The vines were sprayed practically every week as long as the tops continued green, 10 treatments. Doran observed some early blight and tipburn on August 10 and late blight on August 17. Insects were not a limiting factor (Bourne). The yield records were determined from the 2 middle rows of every plot.

On 25 out of 28 plots the fungicides reduced the amount of rot. The Bordeaux was the most effective followed by high and low basic sulfates. The extreme variations in results due to inequalities in soil, natural drainage, excessive rainfall, etc., warrant only general deductions as to trend. The Bordeaux was unquestionably superior to the basic sulfates probably due to its greater dispersion.

Dusting experiments were conducted on the Station rotation 0.08 acre plots Nos. 51, 54 and 57 and on the west half of Field B 0.205 acre plot, under the supervision of J. P. Jones, to determine the relative effectiveness of low and high basic sulfates and a commercial monohydrated copper sulfate-hydrated lime dust in controlling early and late blights on potatoes. On plot 51 potatoes alternate every other year with onions and on plot 57 with tobacco, while on plot 54 potatoes have been grown continuously for five years. These plots received the equivalent of 2500 pounds of 5-8-7 fertilizer an acre. The northern portion of the west half of Field B was in potatoes in 1927 and the southern portion in mangels. Field B received approximately the equivalent of 2000 pounds of 5-8-7 fertilizer an acre. The seed was certified Green Mountain disinfected with corrosive sublimate. The potatoes were planted on May 10 and harvested on September 14 when the vines were nearly dead. The growth during the entire season indicated adequate fertilizer treatment. The vines remained green longer than usual in spite of late blight, probably because tipburn injury was negligible (Jones). The basic sulfates (lots 6 and 7) were mixed with a free-flowing talc, with and without lead arsenate, and contained 5.41 per cent copper and 4.00 per cent arsenic in the first instance and 6.80 per cent copper in the latter. The commercial copper-lime dust was guaranteed to contain 6.80 per cent copper¹ and when mixed with lead arsenate was calculated to contain 5.41 per cent copper and 4.00 per cent arsenic.

¹Actually tested 7.70%.

Table 10. Relative Effectiveness of Low and High Basic Sulfate and Copper-lime Dusts in Controlling Early and Late Blights on Potatoes

Plot	Fungicide	Total Yield	Grade 1		Grade 2		Grade 3		Rotted		Rotted		Gain or loss over check	
			Bu.	Per cent	Bu.	Per cent	Bu.	Per cent	Bu.	Per cent	Bu.	Per cent	Per cent	Per cent
51 D	Low basic sulfate.....	261.0	132.0	49.0	37.0	43.0	16.48	50.00	57.43	57.43	57.43	57.43	57.43	57.43
51 B	High basic sulfate.....	266.0	166.0	34.0	26.0	40.0	15.01	60.40	60.40	60.40	60.40	60.40	60.40	60.40
51 C	Copper-lime dust.....	292.0	188.0	36.0	31.0	37.0	12.67	113.64	63.37	63.37	63.37	63.37	63.37	63.37
51 A	Check.....	225.0	88.0	15.0	21.0	101.0	44.89
54 D	Low basic sulfate.....	217.0	134.0	41.0	37.0	5.0	2.30	32.67	90.57	90.57	90.57	90.57	90.57	90.57
54 B	High basic sulfate.....	203.0	123.0	30.0	26.0	24.0	11.82	31.78	54.72	54.72	54.72	54.72	54.72	54.72
54 C	Copper-lime dust.....	251.0	166.0	32.0	40.0	13.0	5.18	64.36	75.47	75.47	75.47	75.47	75.47	75.47
54 A	Check.....	213.0	101.0	31.0	28.0	53.0	24.88
57 D	Low basic sulfate.....	235.0	152.0	38.0	34.0	11.0	4.68	43.40	77.55	77.55	77.55	77.55	77.55	77.55
57 B	High basic sulfate.....	241.0	157.0	30.0	34.0	20.0	8.30	48.11	59.18	59.18	59.18	59.18	59.18	59.18
57 C	Copper-lime dust.....	257.0	186.0	30.0	29.0	12.0	4.67	75.47	75.51	75.51	75.51	75.51	75.51	75.51
57 A	Check.....	219.0	106.0	32.0	32.0	49.0	22.37
B 4	Low basic sulfate.....	226.0	167.0	30.5	26.0	2.5	1.11	62.29	95.61	95.61	95.61	95.61	95.61	95.61
B 8	Low basic sulfate.....	232.5	162.6	39.4	26.7	3.8	1.63	58.02	93.33	93.33	93.33	93.33	93.33	93.33
B 2	High basic sulfate.....	273.7	181.6	41.9	38.1	12.1	4.42	76.48	78.75	78.75	78.75	78.75	78.75	78.75
B 6	High basic sulfate.....	248.9	172.7	39.4	27.9	8.9	3.58	67.83	81.97	81.97	81.97	81.97	81.97	81.97
B 3	Copper-lime dust.....	269.2	182.9	48.9	33.0	4.4	1.63	77.75	92.27	92.27	92.27	92.27	92.27	92.27
B 7	Copper-lime dust.....	213.4	133.4	44.5	33.6	2.5	1.17	29.64	95.61	95.61	95.61	95.61	95.61	95.61
B 1	Check.....	238.2	119.4	33.7	20.3	64.8	27.20
B 5	Check.....	209.5	99.1	34.9	27.9	47.6	22.72
B 9	Check.....	203.3	90.2	31.8	22.9	58.4	28.73
Average.....		237.8	143.2	35.4	30.0	29.2	12.27

Average Percentage Gain or Loss Over Checks

Low basic sulfate.....	49.28	79.39
High basic sulfate.....	59.80	66.87
Copper-lime dust.....	70.99	78.26

The several dusts were applied every week from June 22 to September 8, twelve treatments. With the exception of the last treatment rain fell within two days following the application, removing most of the dust. The first 6 treatments contained arsenic which was omitted on August 3 and thereafter except on August 23 when the basic sulfates with lead arsenate were applied. Lead arsenate and talc were applied 8 times to the checks which was probably more than was needed. A method of weekly applications is a systematic procedure that is apparently unnecessary early in the season except possibly of lead arsenate for insects, but more frequent applications later in the season following rains might prove more effective in controlling blight (Jones). Doran observed some early and late blights and tipburn on August 17 and considerable late blight on September 10. The yield records were determined from the two middle rows of every 4-row section except the one-half outside sections of Field B, of which both rows were taken.

All the dusts reduced the amount of rot, but the low basic sulfate proved slightly the most effective in this respect. The physical characteristics of fungicides are a factor in the flow and economical coverage when applied as a dust. Neither of the basic sulfates was suitable for application in this form, while the copper-lime dust was light, bulky and of good flow.

Apples

A spraying experiment was conducted on Block B of the Station orchard under the supervision of J. K. Shaw and W. A. Cutler, to determine the relative effectiveness of low and high basic sulfates and lime-sulfur in controlling diseases, primarily scab, on McIntosh and Red Astrachan apples, and the amount of injury to foliage and fruit. The basic sulfates (lots 6 and 7) with lead arsenate and raw linseed oil 1.50-0.50 pt.-50 were applied at a concentration of about 0.07 per cent copper and 0.071 per cent arsenic. A standard mixture of lime-sulfur (33°B) and lead arsenate 1.25 gals.-1.50-50 was employed for comparative purposes. The sprays were applied with a Friend power sprayer with 250-gallon tank, under 275 pounds pressure, and Friend guns with 3/32 disc nozzles. In the pre-pink spray (May 2) and pink spray (May 9) the basic sulfates injured the fruit buds a little more than lime-sulfur. In the calyx spray (May 24) the basic sulfates injured the fruit to some extent, as considerable russetting was observed later, but failed to control scab. Lime-sulfur also gave poor control but proved superior to the basic sulfates and caused less injury. The copper sprays mixed well and their adherence was very good (Cutler). Doran made the following observations as to injury and scab on foliage.

Table 11. Relative Effectiveness of Low and High Basic Sulfates and Lime-sulfur in Controlling Scab on McIntosh and Red Astrachan Apples, and the Amount of Injury,—As Shown by the Foliage

Plot	Fungicide	June 14	July 16
1	Low basic sulfate.....	Leaves yellow and falling badly. Not much scab.	Trees defoliated. Fruit russeted.
2	High basic sulfate.....	Leaves yellow and falling badly. Not much scab.	Trees defoliated. Fruit russeted.
3	Lime-sulfur.....	Leaf injury negligible. Not much scab.	No leaf injury. Fruit not russeted.

Doran noted practically no injury to apple foliage from lime-sulfur, but the basic sulfates defoliated the trees seriously and russeted the fruit. The foliage of the Red Astrachan was injured more than that of the McIntosh.

Table 12. Relative Effectiveness of Low and High Basic Sulfates and Lime-sulfur in Controlling Scab on McIntosh and Red Astrachan Apples, and the Amount of Injury,—As Shown by the Yield

Fungicide	Row	Number of trees	Total yield	Yield per tree
			<i>Lbs.</i>	<i>Lbs.</i>
McIntosh				
Low basic sulfate.....	B	30	228	7.60
High basic sulfate.....	D	29	117	4.03
Lime-sulfur.....	F	30	119	3.97
Check.....			all fruit dropped	
Red Astrachan				
Low basic sulfate.....	A	30	700	23.33
High basic sulfate.....	C	28	673	24.04
Lime-sulfur.....	E	29	1067	36.79
Check.....			all fruit dropped	

Evidently the fungicides were not the limiting factor with McIntosh, but may have had more influence with Red Astrachan.

Doran and Bourne made fruit counts on 1851 McIntosh apples from the several plots on October 8, and obtained the following results:

Table 13. Relative Effectiveness of Low and High Basic Sulfates and Lime-sulfur in Controlling Scab on McIntosh, and Amount of Injury,—As Shown by Fruit Counts

Plot	Fungicide	Clean	Scab	Russet
		Per cent	Per cent	Per cent
1	Low basic sulfate.....	7.59	55.26	68.73
2	High basic sulfate.....	23.90	48.66	43.14
3	Lime-sulfur.....	62.65	28.31	9.44
Check.....			all fruit dropped	

None of the fungicides gave proper control of scab on McIntosh apples under the conditions of operation, which indicates that the applications were improperly timed. From the standpoint of clean fruit and a minimum of russet injury, lime-sulfur was superior to basic sulfates on McIntosh that year.

A dusting experiment was conducted on Block A of the Station orchard, under the supervision of J. K. Shaw and W. A. Cutler, to determine the relative effectiveness of low and high basic sulfates, copper-lime dust and lime-sulfur spray in controlling scab on 5 varieties of apples, and the amount of injury to foliage and fruit. The basic sulfates (lots 6 and 7) were mixed with lead arsenate and a free-flowing talc and contained 3.00 per cent copper and 2.00 per cent arsenic. The copper-lime dust was guaranteed to contain 3.94 per cent copper¹ and 2.92 per cent arsenic. A standard mixture of lime-sulfur (33°B) and lead arsenate 1.25 gals.—1.50–50 was employed for comparative purposes. The dusts were applied with a Niagara power duster and the spray with a Friend power sprayer with 250-gallon tank, under 275 pounds pressure, and Friend guns with 3/32 disc nozzles. The trees on plots 1, 3 and 5 received nitrates while those on plots 2, 4 and 6 did not and were less vigorous and had thinner foliage. In the pre-pink dust (May 7) which was delayed nearly a week on account of the duster being out of order, and the

¹Actually tested 4.28%.

pink dust (May 14) the basic sulfates and copper-lime dust seemed to give similar results with very little burning. In the calyx dust (May 24) none of the dusts was effective in controlling scab. The dusts were applied in the morning when there was very little wind but did not adhere as well as expected (Cutler). Doran made the following observations as to injury and scab on foliage:

Table 14. Relative Effectiveness of Low and High Basic Sulfate Dusts, Copper-lime Dust, and Lime-sulfur Spray in Controlling Scab, and Amount of Injury,—As Shown by the Foliage

Plot	Fungicide	June 14	July 16
0	Check.....	No burning. Scab very severe.	Not much leaf burn. Scab most severe.
1	Low basic sulfate.....	No burning. More scab than with lime-sulfur.	Not much leaf burn. Scab very severe.
2	Lime-sulfur.....	No burning. Scab moderate.	Not much leaf burn. Less scab than with dusts.
3	High basic sulfate.....	No burning. Scab severe on McIntosh.	Moderate leaf burn. Scab very severe.
4	Lime-sulfur.....	No burning. Much less scab than with dusts.	Not much leaf burn. Scab bad.
5	Copper-lime dust.....	No burning. More scab than with lime-sulfur.	Not much leaf burn. Scab severe.
6	Lime-sulfur.....	No burning. Considerable scab on McIntosh.	Not much leaf burn. Less scab than with dusts.

As a whole Doran noted comparatively little injury to apple foliage from either copper dusts or lime-sulfur spray. The high basic sulfate may have been slightly the most injurious. None of the treatments afforded adequate protection to the foliage against scab probably because of too late application and adverse weather conditions. The best control was obtained with lime-sulfur although inconsistent and "bad" on plot 4. Scab was severe or very severe with all dusts and most severe on the check trees. A closer differentiation would require leaf counts which was not attempted. The effect of insects was negligible (Bourne). As all the plots did not receive the same fertilizer treatment the yields were not comparable and are omitted.

Doran and Bourne made fruit counts on 1825 McIntosh apples from the several plots on October 8 and obtained the following results:

Table 15. Relative Effectiveness of Low and High Basic Sulfate Dusts, Copper-lime Dust, and Lime-sulfur Spray in Controlling Scab on McIntosh, and Amount of Injury,—As Shown by Fruit Counts

Plot	Fungicide	Clean	Scab	Russet
		<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
1	Low basic sulfate.....	2.50	97.50	2.50
3	High basic sulfate.....	7.84	91.37	8.24
5	Copper-lime dust.....	14.44	71.66	20.14
2, 4, 6	Lime-sulfur.....	27.66	70.29	3.55
0	Check.....

None of the fungicides gave control of scab on McIntosh apples because of too late application (Shaw). From the standpoint of scab control and a minimum of russet injury, lime-sulfur spray was rather more effective than the copper dusts.

Grapes

Spraying and dusting experiments were conducted in the College vineyard, under the supervision of O. C. Roberts, to determine the relative effectiveness of low and high basic sulfates (lots 6 and 7), Bordeaux 1.17 1.17-50 and a commercial copper-lime-lead arsenate dust in controlling diseases on Worden grapes and the amount of injury to foliage.

The basic sulfates with lead arsenate and linseed oil 1.50-0.83 pt.-50 were applied as sprays at a concentration of 0.07 per cent copper and 0.07 per cent arsenic, the same as Bordeaux 1.17 1.17-50 with lead arsenate 1.50 50. Chemical hydrated lime was employed in preparing the Bordeaux. Oil was used with the arsenic check spray but not with the Bordeaux. The basic sulfates, mixed with lead arsenate and a free-flowing talc, were applied as dusts which contained 3.00 per cent copper and 2.00 per cent arsenic. The commercial dust was guaranteed to contain 3.94 per cent copper¹ and 2.92 per cent arsenic. The arsenical check dust was composed of lead arsenate and talc and contained 2.00 per cent arsenic. The spray was applied under 75 to 100 pounds pressure with a double action, Deming barrel hand-pump equipped with 2 lines of hose to which were attached rods and disc nozzles. The first two applications of dust were made with an American Beauty hand duster which proved unsatisfactory because of its irregular, intermittent discharge. The last application was made with a Peerless duster which gave an even continuous flow.

The fungicides were applied on the following dates and under the weather conditions stated:

June	7—cloudy, humid, 68° Fahr.	Spray and dust.
July	16—clear, moderate southwest wind.	Spray.
July	18—clear, moderate southwest wind, 85° Fahr.	Dust.
August	13—clear, 75° Fahr.	Spray.
August	14—clear, humidity somewhat higher than on the 13th, 76° Fahr.	Dust.

Doran found a little downy mildew in the vineyard on August 22 and observed traces on the check plot on September 11. No black rot was detected at any time. As there was practically no disease during the season the efficiency of the several fungicides could not be determined. Bourne noted a few leaf hoppers in the vineyard uniformly distributed over the plots.

Doran, Bourne and Roberts made the following observations on September 21 and 25 relative to foliage injury:

Low basic sulfate spray—burn practically the same as for high basic sulfate, adherence good.

High basic sulfate spray—more burn than on check plot, spray residue adhered well to fruit.

Bordeaux—burn less than from basic sulfates, adherence good.

Check—spray burn mild and generally distributed.

Low basic sulfate dust—burn practically the same as high basic sulfate.

High basic sulfate dust—no more burn than on check plot.

The yield had no significance due to pilfering of the fruit and is omitted.

In the practical absence of disease little could be learned of the relative value of the fungicides. The commercial copper-lime-lead arsenate dust was sticky and would not flow freely (Roberts).

Discussion of Results

The results of the four years of field work appear to warrant the following deductions as to the effectiveness of basic copper sulfate in controlling diseases on various garden crops and fruits and the amount of injury likely to ensue.

¹Actually tested 4.28%.

Cucumbers—Low basic sulfate spray (0.25 per cent Cu) was equal or superior to Bordeaux (0.25 per cent Cu) in controlling anthracnose and powdery mildew on cucumbers as determined by yield in 1925 and by leaf counts in 1926. Both fungicides appeared to be slightly injurious to the young leaves in 1926. Neither spray (0.26 per cent Cu) nor dust (7.02 per cent Cu) application of high basic sulfate afforded protection under the continuous heavy rains of 1927, although the dust was slightly the more effective. Neither caused injury.

Celery—Low basic sulfate spray (0.25 per cent Cu) was equal to Bordeaux (0.25 per cent Cu) in controlling early and late blights on celery as determined by yield in 1925 and by leaf counts in 1926. Both spray (0.26 per cent Cu) and dust (7.02 per cent Cu) applications of high basic sulfate increased the yield and grade of celery in 1927, but the dust proved the more effective. Low and high basic sulfate sprays (0.24 per cent Cu) were fully equal to Bordeaux (0.24 per cent Cu) and superior to low and high basic sulfate dusts (6.80 per cent Cu) on celery in 1928 as determined by yield, although the experiment has little significance as the plants did not reach marketable size due to adverse weather conditions.

Potatoes—Low basic sulfate spray (0.26 per cent Cu) was not equal to Bordeaux (0.25 per cent Cu) in controlling early and late blights on potatoes, as determined by yield in 1926; nor was high basic sulfate spray (0.25 per cent Cu) in 1927. Tuber rot, however, did not exceed 1 to 2 per cent in either case (Doran). Low and high basic sulfate sprays (0.24 per cent Cu) were not equal to Bordeaux (0.24 per cent Cu) on potatoes in 1928 as determined by yield of grade No. 1 and by reduction in amount of rot. Evidently a spray of 0.24 per cent copper derived from basic sulfate is not fully adequate to prevent late blight and tuber rot on low lands in a wet season. This was true also of Bordeaux on the College farm in the wet season of 1927, when the rot averaged from 20 to 25 per cent by count. With high basic sulfate dust (7.52 per cent Cu), there was about 1 per cent by weight of tuber rot in 1927. There were no checks. Low and high basic sulfate dusts (6.80 per cent Cu) were not equal to a copper-lime dust (7.70 per cent Cu) on potatoes in 1928, as determined by yield of grade No. 1 and by reduction in amount of rot collectively. The low basic sulfate dust, however, in spite of a lower copper content reduced rot rather more than the copper-lime dust.

Fruits—Low basic sulfate sprays (0.13, 0.19 and 0.25 per cent Cu) were not equal to standard lime-sulfur in controlling scab on Baldwin and McIntosh apples in 1926, and injured the foliage and russeted the fruit, especially in the higher concentrations. The injury on the foliage of Monarch plums increased with the concentration, but was not appreciable on the fruit. With mixed high and low basic sulfate sprays (0.06 and 0.19 per cent Cu) and with lime-sulfur, there was about the same percentage of scabby fruit on Baldwin and McIntosh apples in 1927. The dilute spray with linseed oil was no more injurious than lime-sulfur and was reported a promising mixture for apples (Cutler). The concentrated spray killed the buds and injured the leaves. With mixed high and low basic sulfate dusts (2.50 and 5.00 per cent Cu) on McIntosh apples and Bartlett pears in 1927, there were only a few scab spots on McIntosh with the dilute mixture. Both dusts caused a small amount of russet on McIntosh but no foliage injury. The copper content was reported about right (Drain). Low and high basic sulfate sprays (0.07 per cent Cu) were not equal to lime-sulfur in controlling scab on McIntosh and Red Astrachan apples in 1928 as determined by fruit counts on McIntosh, although none of the fungicides gave adequate control, probably because of too late application. The basic sulfates defoliated the trees seriously and russeted the fruit more than lime-sulfur. Low and high basic

sulfate dusts (3.00 per cent Cu) and a copper-lime dust (4.28 per cent Cu) were not equal to lime-sulfur in controlling scab on Baldwin, McIntosh, Northern Spy, R. I. Greening and Tompkins King apples in 1928 as determined by fruit counts on McIntosh, although none of the fungicides gave satisfactory control on either fruit or foliage, probably because of too late application. Basic sulfate dusts did not injure the foliage appreciably, but russeted McIntosh apples a little more than lime-sulfur.

The effectiveness of low basic sulfate sprays (0.13, 0.19 and 0.25 per cent Cu) on Moore's early grapes in 1926 could not be determined in the absence of disease. The injury to foliage increased with the concentration but was not appreciable on the fruit (Roberts). The relative effectiveness of spray (0.06 and 0.19 per cent Cu) and dust (2.50 and 5.00 per cent Cu) applications of mixed basic sulfates and of Bordeaux (0.24 per cent Cu) in controlling mildew and black rot on Worden grapes in 1927 could not be determined, as practically no disease developed. The leaves remained green 10 to 14 days longer with basic sulfates than with Bordeaux, and complete defoliation was equally delayed. The dilute dust caused practically no injury to the foliage, the dilute spray a little, the concentrated dust and spray considerable and Bordeaux most of all. With the latter the "burned" condition was decidedly apparent. Low and high basic sulfate sprays (0.07 per cent Cu) and dusts (3.00 per cent Cu) and dilute Bordeaux (0.07 per cent Cu) were applied to Worden grapes in 1928, but their effectiveness could not be determined in the absence of disease. There was some foliage injury without marked differences. The least was probably on the check, followed by the basic sulfate dusts, Bordeaux and basic sulfate sprays.

Low basic sulfate spray (0.25 per cent Cu) was applied to currants, English gooseberry, nine varieties of grapes, tea roses and phlox in 1926 without injury being observed (Brooks). Low basic sulfate spray (0.16 per cent Cu) did not injure rhododendron seedlings in flats (Kinney).

As to supplementary products, Wilkinité proved of little value except possibly to increase visibility. Saponin was of value in increasing wetting and spreading, and raw linseed oil in increasing adhesiveness. The oil was the most promising. It mixed well and the spray residue adhered firmly to the foliage and fruit of apples and grapes (Cutler, Roberts); while on cucumbers, celery and potatoes, oil was not approved (Guba, Cubbon). The dusts with talc as the vehicle distributed well (Guba, Drain) and appeared to have good adherence (Drain).

Summary and Conclusions

1. Commercial basic copper sulfate has proved effective in controlling disease on cucumbers and celery and promising on potatoes, but requires further demonstration on orchard fruits and grapes.
2. A greater "copper" concentration of basic sulfate than of Bordeaux is necessary in some instances to assure equal control, due to the lower dispersion.
3. The low basic sulfate appears to be slightly more effective per unit of copper than the high basic sulfate, probably because the physical condition has averaged better.
4. The concentration necessary in sprays differs widely from that needed in dusts, as the large proportion of inert vehicle in dusts depresses the activity of the fungicide. The following concentrations of basic copper sulfate and of lead arsenate in sprays and dusts are suggested tentatively for field practice.

Crop	Sprays		Dusts	
	Cu	As	Cu	As
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
Apples.....	0.05	0.07*	3.50	2.00
Grapes.....	0.05	0.07	3.50	2.00
Celery.....	0.30	7.50
Cucumbers.....	0.25	0.09**	7.50	4.00
Potatoes.....	0.30	0.09	7.50	4.00

*1.50—50.

**2.00—50.

5. Basic sulfate is insoluble and slowly available and must be applied at the proper time and concentration to insure protection.

Literature Cited¹

1. Bell, J. M., and Taber, W. C.
1908. The three-component system—CuO, SO₃, H₂O—at 25°. Jour. Phys. Chem. 12:171-179.
2. and Murphy, G. M.
1926. Basic copper at 100°. Jour. Amer. Chem. Soc. 48 (1): 1500-1502.
3. Britton, H. T. S.
1925. Electrometric studies of the precipitation of hydroxides. Pt. IV. Precipitation of mercuric, cadmium, lead, silver, cupric, uranic and ferric hydroxides by the use of the oxygen electrode. Jour. Chem. Soc. [London] 127 (2): 2148-2159.
4.
1925. An electrometric and phase rule study of some basic salts of copper. Jour. Chem. Soc. [London] 127 (2): 2796-2807.
5. Field, F.
1862. On some of the basic salts of copper. Phil. Mag. and Jour. Sci. (4) 24:123-126.
6. Holland, E. B., Dunbar, C. O., and Gilligan, G. M.
1926. The preparation and effectiveness of basic copper sulphates for fungicidal purposes. Jour. Agr. Research 33:741-751.
7. Kane, R.
1839. Ann. Chim. et Phys. (2) 72:269.
8. Kruger, —.
1924. Jour. Prakt. Chem. 108:278.
9. Nelson, O. A.
1928. Effect of alkalinity on basic cupric sulphates. Jour. Phys. Chem. 32:1185-1190.
10. Pickering, S. U.
1907. The interaction of metallic sulphates and caustic alkalis. Jour. Chem. Soc. [London] 91 (2): 1981-1988.
11.
1910. The constitution of basic salts. Jour. Chem. Soc. [London] 97 (2): 1851-1860.
12. Proust, J. L.
1800. Recherches sur le cuivre. Ann. Chim. et Phys. (1)32:26-54.

¹The original articles were not always available.

13. Reddick, D., and Wallace, E.
1910. On a laboratory method of determining the fungicidal value of a spray mixture or solution. (Abstract) Science (n. s.) 31:798.
14. Sabatier, P.
1897. Compt. Rend. Acad. Sci. [Paris] 125:101.
15. Smith, J. D.
1843. On the constitution of the subsalts of copper. No. 1. On the subsulphates. Phil. Mag. and Jour. Sci. (3) 23:496-505.
16. Vogel, A., and Reischauer, C.
1859. Jahresber. Pharm. 11:3.
17. Williamson, F. S.
1923. Basic copper sulphate. Jour. Phys. Chem. 27:789-797.
18. Young, S. W., and Stearn, A. E.
1916. The basic copper sulphates. Jour. Amer. Chem. Soc. 38 (2):1947-1953.

